A Test of Limnological Data from the Experimental Lakes Area, Northwestern Ontario, for Evidence of Acidification

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ABSTRACT

Schindler, D.W., and T. Ruszczynski. 1983. A test of limnological data from the Experimental Lakes Area, northwestern Ontario, for evidence of acidification. Can. Tech. Rep. Fish. Aquat. Sci. 1147: iv + 17 p.

Two older (1967 and 1973) data sets were compared with 1978 survey information in order to detect possible acidification of lakes near the Experimental Lakes Area of northwestern Ontario. An error in analysis or calculation in the 1973 data set precluded reliance on measured alkalinity, the most sensitive indicator of lake acidification. Calculated alkalinity, conductivity and pH showed no conclusive evidence of acidification, although watershed modifications, both human and natural, during the period provided confounding influences on the parameters examined. Long-term data sets for several lakes also showed no conclusive evidence of acidification due to precipitation of current pH values (average pH 4.9-5.0).

Key words: lake acidification; acid precipitation.

RESUME

Schindler, D.W., and T. Ruszczynski. 1983. A test of limnological data from the Experimental Lakes Area, northwestern Ontario, for evidence of acidification. Can. Tech. Rep. Fish. Aquat. Sci. 1147: iv + 17 p.

Deux plus anciennes séries de données (1967 et 1973) ont été comparées aux renseignements recuillis lors de l'étude de 1978, afin de déterminer l'acidification éventuelle des lacs qui se trouvent à proximité de la Région des Lacs Expérimentaux dans le nord-ouest de l'Ontario. Une erreur dans les analyses ou les calculs dans la série de données de 1973 n'ont pas permis de nous baser sur l'alcalinité mesurée, indice le plus sensible d'acidification. L'alcalinité calculée, la conductivité et le pH ne montrent aucune preuve conclusive d'acidification, bien que les modifications de bassins hydrographiques naturels et artificiels, au cours de la période, témoignent, sur les paramètres examinés, d'influences qui nous laissent perplexes. Des séries de données à long terme pour plusieurs lacs ne montrent pas non plus de preuve conclusive d'acidification due à la précipitation des valeurs de pH courantes (pH moyen 4.9-5.0).

Mots-clés: acidifications des lacs; précipitation acide.

INTRODUCTION

Recent studies have shown that large numbers of lakes in non-calcareous terrain are becoming acidified due to acid deposition (Wright and Snekvik 1978; papers in Drablos and Tollan 1980).

In Canada, Dillon et al. (1978) discovered that lakes in the Haliburton and Muskoka districts of eastern Ontario, where precipitation currently has an average pH of 4.1-4.2, had lost a high proportion of their alkalinity in the previous 5 to 10 years. In an area with equally acid precipitation near Sudbury, Ontario, the hydrogen ion concentration of lakes increased ten-fold or more in ten years (Harvey 1980). Near Halifax, Nova Scotia, where precipitation has an average pH of about 4.6, Watt et al. (1979) found slight but significant decreases in the pH of lakes between 1955 and 1977. Thompson et al. (1980) reported similar decreases in the pH of Nova Scotian rivers.

Scandinavian studies have shown that acidification of lakes is only detectable where the precipitation has a pH of 4.7 or less (Henriksen 1979). Similar results have been reported from Scotland (Wright et al. 1980). The above observation has led to a recent recommendation (NRC 1981) that the hydrogen ion concentration of precipitation should be reduced enough to cause average pH values to exceed 4.7.

However, there have been no analyses of long-term data sets in regions where the precipitation is less acid than pH 4.7. There is considerable interest in such information, because of the fear that remote wilderness areas subjected to even small increases in atmospheric pollutants may be slowly deteriorating, for example, the Boundary Waters Canoe Area of northeastern Minnesota, where precipitation currently averages about pH 5.0, but where low pH "episodes" accompany the runoff of spring melt water into lakes (Glass and Loucks 1980).

The purpose of this work was to compare recent measurements of acidity and several acid-related parameters in small lakes of the Experimental Lakes Area (ELA) of northwestern Ontario (lat. 49°30' to 49°45'N, long. 93°30' to 94°00'W) with older measurements, in order to see if there is any tendency for the lakes to become more acid. The assumption that natural lakes in the area are more or less at steady state with respect to precipitation acidity is also an assumption fundamental to the interpretation of whole lake acidification experiments (Schindler 1980; Schindler et al. 1980a). Bulk precipitation in the area has had an average pH of 4.90 to 5.00 for 8 out of 9 years between 1970 and 1980 (Table 1). Corresponding sulfate deposition rates have averaged 8.6 kg ha^{-1} for the period, with no tendency to increase. While a number of unforeseen pitfalls hindered the anticipated interpretation of the data, we believe that our attempts to investigate the shortcomings of the available data set will prove instructive to others who are trying to assess long-term acidification of lakes.

MATERIALS AND METHODS

In fairness to the older studies which we analyzed, it must be pointed out that the authors did not design them for the purpose of detecting acidification.

Cleugh and Hauser (1971) reported surface water conductivities for several hundred lakes in the ELA area. Because of the high specific conductance of the hydrogen ion, conductivity is sensitive to changes in acidity. It is, however, also affected by changes in ionic strength from other ions. In 1973, Beamish et al. (1976) determined surface water pH, conductivity, alkalinity and major ions for 109 lakes of the area. Both of the above studies were done in late summer (August-September). Beamish et al. measured hydrogen ion concentration both in the field and immediately upon return to the laboratory. Alkalinities were measured in the laboratory by summer field staff. While details of the procedures for pH, conductivity and alkalinity were not recorded, meters were carefully calibrated with fresh buffer solutions, and titrations were done to fixed end points (R.J. Beamish and G.A. McFarlane, pers. comm.). All other chemistry was done at the Freshwater Institute, by the methods of Stainton et al. (1977).

On May 12 and September 8, 1978, we surveyed 98 and 101 small ELA lakes, respectively, using a helicopter to obtain samples near the center of each lake. The May survey was done just after spring overturn; the September one late in the summer stagnation period. The surface areas of the lakes sampled ranged from 0.5 to 300 ha and maximum depths ranged from 1-33 m with the exception of Teggau Lake (L228) which had an area of 1676 ha and a maximum depth of 170 m.

A 500 mL polyethylene bottle and a 50 cc plastic syringe were filled at a depth of about 0.5 m in each lake. A mercury thermometer was immediately inserted in the 500 mL bottle, to obtain *in situ* lake surface temperature. Each survey was completed in a single day.

Conductivity, dissolved inorganic carbon (DIC) and pH were analyzed from the 50 cc syringe within a few hours of collection (Stainton et al. 1977). The 500 mL bottle was stored at 5°C for subsequent calcium analyses by atomic absorption (Stainton et al. 1977) and alkalinity was measured by a closed-vessel titration and Gran plot as described by Stumm and Morgan (1970). Gran plots were done for the pH range 4.8-4.2. These values are designated (Alk_m) to distinguish them from calculated alkalinities (Alk_c). Calculated alkalinities were calculated by partitioning the DIC and using the equation:

$$(1) \quad Alk_c = HCO_3^- + 2CO_3^{-2} + OH^- - H^+,$$

where H^+ is the *in-situ* value.

Three pH values were recorded. "Laboratory pH" measurements, from the 50 cc syringe, were obtained within two hours of sampling at

laboratory temperature. In addition, an "in situ" pH was calculated according to the following equation:

$$(2)\quad \frac{H^+ Alk_m - K_w + (H^+)^2}{H^+ + 2K_2} = \frac{DIC \quad K_1 \quad H^+}{(H^+)^2 + K_1H^+ + K_1K_2}$$

where Alk_m is assumed to equal
$HCO_3^- + 2CO_3^= + OH^- - H^+$
DIC is the measured dissolved inorganic carbon
K_1 and K_2 are the first and second dissociation constants of carbonic acid, and
K_w is the dissociation constant of water.

Equation (2) is then solved for $[H^+]$, using measured alkalinities and DICs:

$$(3)\quad 0 = [H^+]^4 + A[H^+]^3 + B[H^+]^2 + C[H^+] + D$$

where $A = Alk_m + K_1$
$B = K_1 Alk_m + K_1K_2 - K_w - K_1DIC$
$C = K_1K_2 Alk_m - 2K_1K_2DIC - K_1K_w$
$D = -K_1K_2K_w$
and K_1, K_2 and K_w are adjusted for in-situ temperature.

An "equilibrium pH", the pH in air equilibrated with atmospheric CO_2, was also measured. This was measured immediately after bubbling the sample with outdoor air pumped through a polyethylene bubbling frit for 20 minutes.

The Calcite Saturation Index (CSI) (Conroy et al. 1974) provides a quantitative estimate of a lake's resistance to acidification and is defined as:

$$(4)\quad CSI = p(Ca) + p(Alk) - p(H^+) + pk$$

where $p(x) = \log_{10}(x)$
$pk = +2$, and
Ca, Alk and H^+ are in mol l^{-1}.

Our calculations were done using measured alkalinities and laboratory pH values. In waters saturated with $CaCO_3$, CSI = 0; if supersaturated, CSI<0. Conroy et al. (1974) consider lakes with CSI's greater than 4, and possibly those greater than 3, to be susceptible to acidification.

RESULTS

THE 1978 SURVEYS

Laboratory pH values of surveyed lakes ranged from 5.18 to 7.01 for the spring survey and 5.39 to 7.59 for the late summer survey (Fig. 1). Ranges for conductivity, DIC, calcium and alkalinity are shown in the table below.

Regression analyses of "calculated alkalinities" from equation 3 vs alkalinities measured by Gran plot yielded regressions of: Meas. alk = 1.02 calc alk + 7.31 and Meas. alk = 1.11 calc alk + 9.97 for the spring and late summer surveys, with r values of 0.95 and 0.97, and n = 91 and 94 respectively. The spring slope did not significantly differ from 1.00, while the fall slope did (P = 0.05), suggesting that factors other than bicarbonate contributed slightly to late summer alkalinity.

	Spring Survey	Late Summer Survey
Conductivity μmho cm^{-1}	13.1 - 31.7	13.0 - 35.0
DIC μM l^{-1}	57 - 245	34 - 255
Ca, μeq l^{-1}	40.5 - 167	7 - 187
Meas. alk, μeq l^{-1}	0 - 159	35 - 224
CSI	3.1 - 10.4	2.7 - 6.4

Frequency distributions are given in Fig. 2.

Fifty percent of the surveyed lakes had CSI values greater than 4. Only two values less than 3 were recorded, both in the late summer survey. The waters are thus extremely vulnerable to acidification.

pH CHANGES FROM 1973 TO 1978

Seventy-one of the lakes surveyed in September 1978 had also been surveyed by Beamish et al. (1976) in September 1973. "Laboratory pH" values appear to have been measured by comparable methods in both surveys. Approximately 70% of the lakes either had no change or an increase in pH over the period. The mean pH change for all lakes was +0.15 units over the period (Fig. 3). Student's t test for paired observations revealed that this increase was significant (P = 0.01).

However, not all of the 71 lakes were unmodified during the five year period. Disturbances affecting some of the watersheds between 1973 and 1978 included a major windstorm in 1973, a forest fire in 1974, and clear-cut logging throughout the period. Any of these influences will affect the chemistry of inflow waters to the lakes by increasing chemical concentrations (Schindler et al. 1980a and unpublished). These "modified" lakes are distinguished in Fig. 3. Of the 19 basins which were not influenced by any of the above disasters, 13 (68%) had a slight pH decrease during the period. When unmodified lakes were tested separately, the decrease was not significantly different from zero at the 1% level. When the single high point ($\Delta pH = 1.0$) was eliminated, conclusions did not change.

ALKALINITY CHANGES FROM 1973 to 1978

Beamish et al. (1976) measured alkalinities by potentiometric titration for low alkalinity waters, using an open beaker (American Public Health Association 1976). To test whether results of this method were comparable to those obtained by the closed-cell Gran procedure employed in 1978, we titrated epilimnion samples from seven lakes by both methods. A regression equation yielded the result Gran = 1.00 Potentiometric +4.14 with r = 1.00, and we concluded that in competent hands, the two methods gave comparable alkalinity values, with

the Gran values slightly, but consistently higher.

However, when 1973 and 1978 measured alkalinities were compared, the latter averaged only 0.43 of the former. Nearly all lakes showed the same apparent decrease in alkalinity, including those less susceptible to acidification. This result is inconsistent with the observed total lack of decrease in pH, suggesting a measurement or calculation error in the results of Beamish et al. McFarlane (pers. comm.) discovered an error in the alkalinity calculation procedure for 1976, and supplied recalculated alkalinity data. These still suggested a decrease of 17% during the period (Fig. 4). Their alkalinity data were therefore checked as follows:

Alkalinity values for 1973 were also calculated by ion balance, using other data given in Beamish et al. (1976). Alkalinity can be calculated as the charge difference between nonphotolytic cations and anions or:

$$(5)\quad Alk = (Na^+) + (K^+) + (Ca^{+2}) + (Mg^{+2}) + (Fe^{+2}) + (Mn^{+2}) + (NH_4^+) - (Cl^-) - (SO_4^{-2}) - (NO_3^-)$$

Beamish et al. (1976) reported data for all of the above ions for the 1973 survey, so that it was possible to calculate the alkalinity by equation 5. They also reported DIC values, which we partitioned using the H^+ ion concentration in order to calculate alkalinity, as described in equation 1. Because they did not report lake temperatures from their 1973 survey, a value of 18.4°C, the average for the September 1978 survey, was used for the partitioning.

The average 1973 alkalinity calculated from major ions (equation 5) was 0.53 times the measured one for the same water samples reported by Beamish et al. (1976) (n = 109). The average alkalinities calculated by partitioning the DIC (equation 1) were 0.52 of the reported average measured values, and were in excellent agreement with those calculated by ion balance. Hence, we concluded that 1973 measured alkalinities were erroneous and that no comparison of changes in measured alkalinity between 1973 and 1978 was possible.

Complete ionic analyses were not done on 1978 water samples. As a result, the only comparison of 1978 and 1973 alkalinities which was possible was by partition of DIC (equation 1). Alk_c for 1973 and 1978 were compared by paired t test. The mean Alk_c was 0.83 μeq l^{-1} higher in the latter year, but the difference was not significant at the 1% level.

CONDUCTIVITY CHANGES BETWEEN 1967, 1973, AND 1978

Conductivities in 76 lakes were measured in 1967 and 1978. In 74 lakes, conductivities were done in both 1973 and 1978. Paired t tests revealed an average increase of 3.3 μmhos cm^{-1} between 1973 and 1978, an average decrease of 1.8 μm between 1967 and 1973, and a decrease of 1.5 umhos between 1967 and 1978. The increases from 1967-78 and 1973-78 were significant at the 1% level. An empirical analysis of pH and conductivity results from experimentally acidified Lake 223 indicates that if such changes were due to sulfuric acid addition, the above conductivity changes would represent maximum pH decreases of 0.1 and 0.05 units between 1973 and 1978, and 1967 and 1978, respectively. These are scarcely greater than the probable error in pH measurement. Our other studies (Schindler, unpubl. data) show that conductivity increases may also be caused by other influences on ionic strength, such as clearcutting, burning, roadbuilding, or concentration by evaporation from the lake surface during periods of drought.

ANALYSIS OF LONG-TERM TRENDS

A few "control" lakes have been sampled routinely for a period of several years. Most regularly sampled was Lake 239, where pH, DIC, temperature and conductivity were sampled continuously for eleven years. Lake 240 was sampled for eight of ten years, Lake 302S for six years out of seven, Lake 224 six years in a row, Lake 305 four times in ten years, and Lakes 120 and 129 three years out of eight. For all lakes, the late summer alkalinity of epilimnion water was calculated from DIC, temperature and pH as described above, then regressed on time.

Two "control" basins with low alkalinities had significant decreases with time. Lake 302S, with a calculated alkalinity of 64 μeq l^{-1} in August of 1972, lost an average of 5.4 μeq l^{-1} a^{-1} ($r = 0.88$, Fig. 5). Lake 129, with an alkalinity of 83 in 1971, decreased an average of 4.0 ueq l^{-1} a^{-1} until 1978 ($r = 0.95$). Lake 120 (alkalinity = 70 μeq l^{-1} in 1970) had alkalinity of 44-54 μeq l^{-1} between 1971 and 1974. In 1978, its alkalinity was 59 μeq l^{-1}. There were no significant trends in the alkalinities of other lakes.

DISCUSSION

The aerial surveys of nearly 100 lakes in the ELA area produced no evidence of decline in alkalinity or pH, although due to perturbations in the drainage basins of some lakes, and an analytical error of unknown magnitude in earlier data, the surveys were not as sensitive as originally hoped.

The long-term data sets for several lakes are also affected by changes in the lakes or their watersheds. The only lakes to show consistent alkalinity losses over the period were 302S and 129, and it appears worth scrutinizing those results in more detail. In the case of 302S, the lake served as a control for 302N, as second basin of the same lake to the hypolimnion of which a nutrient mixture containing phosphoric acid, ammonium chloride and sucrose was added in 1972-1976 (Schindler et al. 1980b). From 1972 through August, 1974, no curtain separated the two basins, and water flow between them was unrestricted. Although thermal stratification hindered transport of chemicals from the north to the south basin, during overturn considerable transfer took place, as shown by

increasing chloride concentrations in the South Basin.

Calculations of the nitrogen budget for 302N revealed that most of the nitrogen added as ammonia was permanently removed to the sediments. Charge-balance considerations involved in uptake of ammonia by phytoplankton (Goldman and Brewer 1980) indicate that such removal will leave hydrogen ion in solution, i.e. the situation is analogous to adding hydrochloric acid to the lake:

$$NH_4Cl \longrightarrow NH_3 + H^+ + Cl^-.$$

$\downarrow$

via phytoplankton to sediments

Over the years of study, Cl^- concentrations increased from 0.3 to 1.8 mg L^{-1} in 302S, a change of 42 $\mu eq\ l^{-1}$. If each chloride ion transported from 302N to 302S was accompanied by a hydrogen ion, this would account for the observed alkalinity loss during that period, within error of measurement.

The basins of L120 and 129 were partly logged in 1974. Roughly half of the basins of Lakes 239 and 240 were windthrown in 1973, and burned in a forest fire in 1974. Preliminary calculations indicate that all of these changes increase the yields of all ionic species and of water from the basins. As a result, little or no effect on the pH of lakes might be expected, although this may depend on watershed characteristics. Of all of the basins with measurements spanning several years, only Lake 305 has had neither disturbances in the watershed nor chemical additions to the lake. It shows no evidence of alkalinity change.

Altogether, available evidence suggests that ELA lakes have not become more acid in recent years. If alkalinity is being lost, it is certainly on a time-scale which would require several decades for biologically - significant pH or alkalinity changes to take place. This conclusion must be tentative, because low-alkalinity lakes undergo marked seasonal and year to year changes in alkalinity, caused by differences in hydrology or biological productivity. It therefore appears that current deposition rates of acidifying substances are not harming lakes of the area, although the balance between alkalinity of sensitive lakes and current deposition pattern appears to be a fairly precarious one, as shown by the low, but widely fluctuating alkalinities. Any substantial increase in deposition of acidifying substances in the future would be expected to cause this balance to be upset.

METHODS FOR DETECTING SIGNIFICANT CHANGES IN pH AND ALKALINITY

For a number of reasons, care must be taken in designing surveys for relatively uncontaminated Precambrian Shield lakes, in order to ensure that results are comparable.

pH is highly susceptible to changes in P_{CO_2} of the water in the range 5 to 6, because there is neither alkalinity to buffer the system, as at higher pH values, nor acidic aluminum species, as at lower pH (Johanneson 1980). P_{CO_2} of surface waters can be greatly affected by slight changes in thermal stratification, primary production, or weather. The pCO_2 among lakes of the area in midsummer can range from 0.5 to 2x saturation with the atmosphere (R. H. Hesslein, pers. comm.). The difference can account for several tenths of a pH unit.

This fact is illustrated in Fig. 6, using 1978 survey data, by plotting (ΔpH), the difference between "laboratory pH", where pCO_2 is approximately the in situ value, and "equilibrium pH", after bubbling to a pCO_2 equal to atmospheric saturation, vs pH.

For the spring survey, when most lakes are supersaturated with CO_2 due to metabolic releases of the gas under ice, equilibrating samples with the atmosphere consistently raises the pH.

Results from the late summer survey are quite different. Surface waters of stratified lakes in August-September tend to have lower pCO_2's than in spring, with many lakes below saturation with the atmosphere. On the other hand, in shallow lakes where thermocline erosion has begun to entrain CO_2-rich hypolimnion water by late summer, surface waters may be supersaturated. When the pCO_2 of water is greater than atmospheric, equilibration with air generally results in an increase in pH.

CONCLUSIONS

Although the sensitivity of analyses is decreased by problems with uncertain earlier data, and to the confounding effects of fire, windstorm, clear-cut logging and experimental manipulation, it is impossible to detect any tendency for these poorly-buffered lakes of northwestern Ontario to become more acid over a 5 to 10 year period. If any lake acidification due to acid precipitation is occurring, its effects are presently very slight, and undetectable from the present data base. This finding supports the hypothesis of Henriksen (1979) and the recommendation of NRC (1981) that detectable acidification of sensitive lakes on a time-scale of years to decades only occurs where precipitation pH values of 4.7 or less occur. The slight, but significant decline in lake pH found over 22 years by Watt et al. (1979), in a region of eastern Canada where precipitation has a pH of 4.6-4.7, further indicates that the threshold for detectable effects is near that precipitation pH value. Care must be taken by managers of northwestern Ontario airsheds to ensure that there is no increase in acid precursors in the area, because average precipitation pH values of the area are already as low as 4.9-5.0.

Future surveys designed to detect the long-term effects of acid precipitation on lakes

must be designed to eliminate variations due to analytical procedures. We believe that all pH measurements should be taken with pCO_2 at equilibrium with outside air (laboratory air tends to be greatly oversaturated with CO_2). Alkalinity measurements should be by closed-cell titration and Gran plot, using only carefully calibrated acids, burettes and pH meters. As illustrated here, an erroneous set of measurements will obscure any trend in acidification. Complete ionic chemistry and DIC analyses should be done in order to provide a check on alkalinities.

Measurements should be done frequently, preferably seasonally, in order to detect the effects of year-to-year changes in hydrology or stratification. Drainage basins should be characterized, with the occurrence of human disturbance and natural disasters over the years of study carefully recorded.

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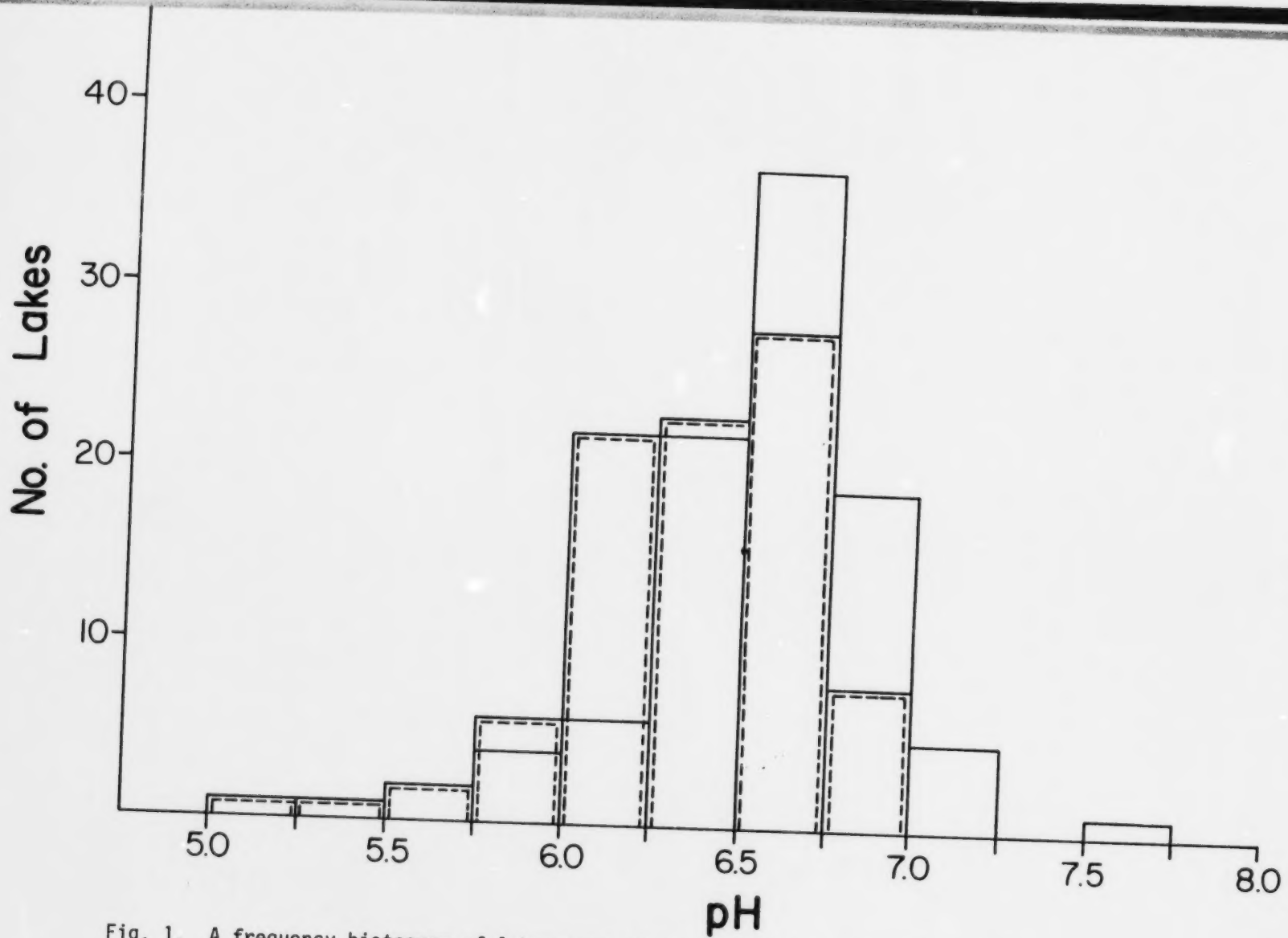

Fig. 1. A frequency histogram of laboratory pH for both May and September, 1978 surveys. ═══ represents May values; ——— represents September values. N = 91 and 95 respectively.

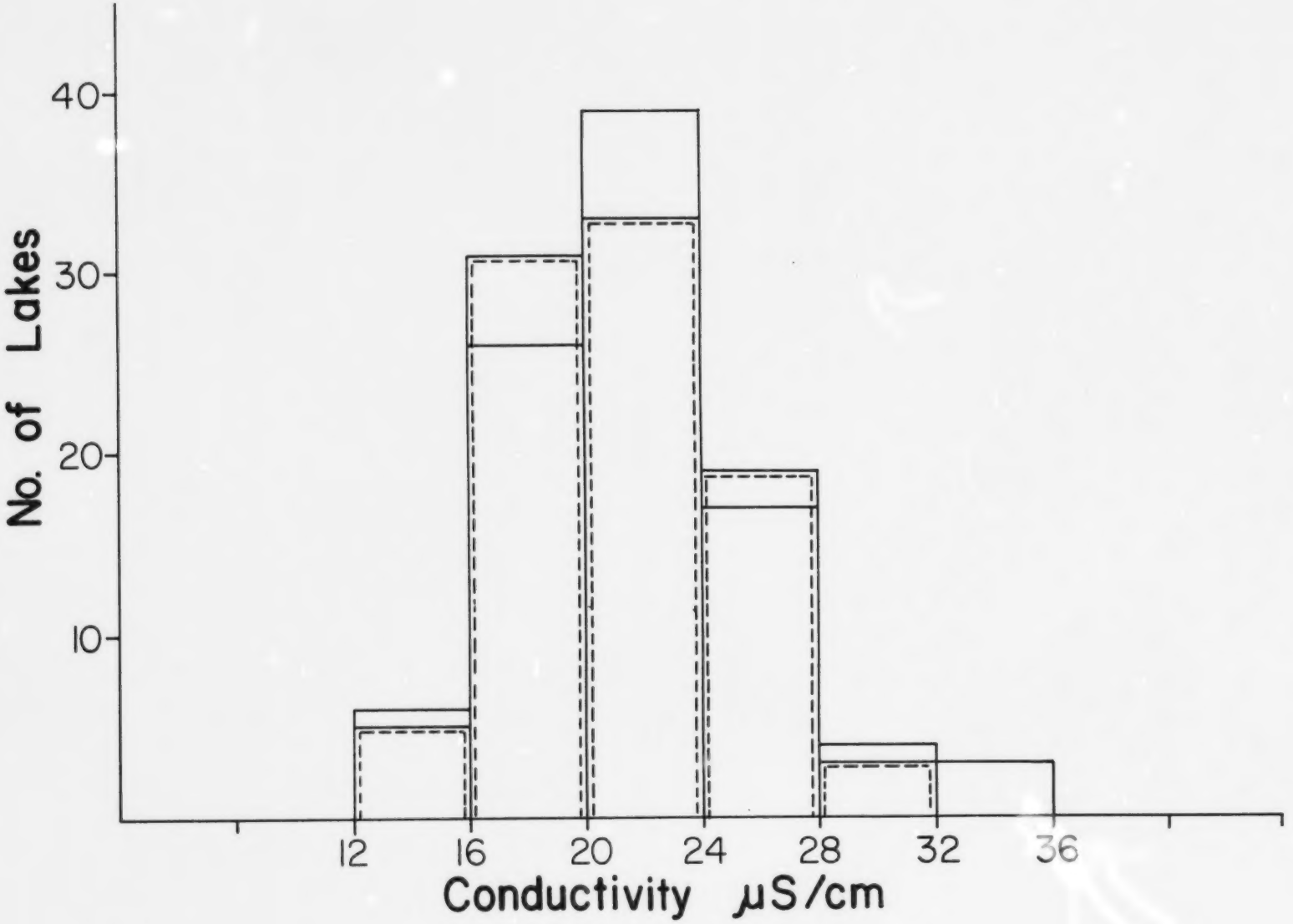

Fig. 2a. Frequency histogram of conductivity. Legend as in Fig. 1.

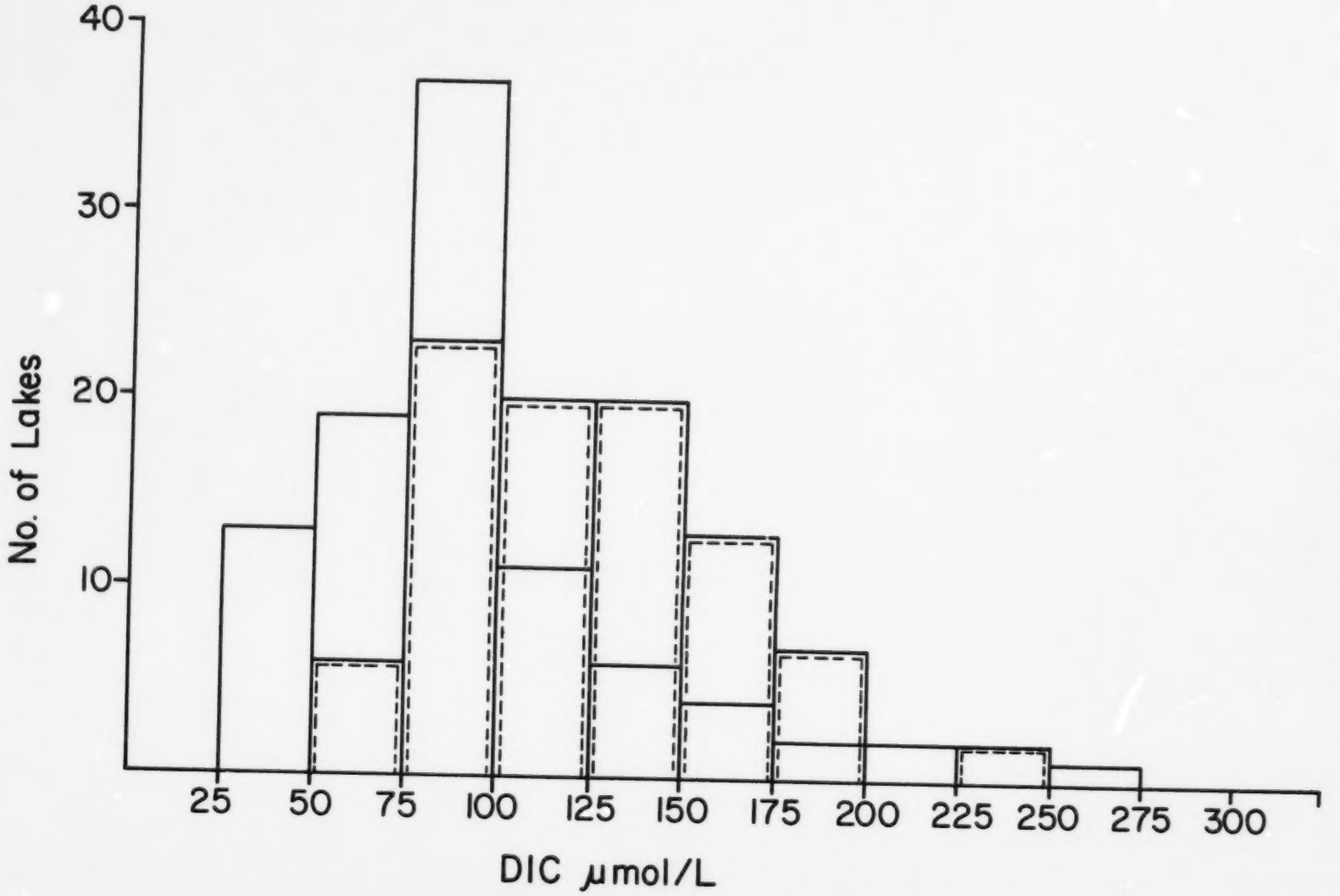

Fig. 2b. Frequency histogram of DIC. Legend as in Fig. 1.

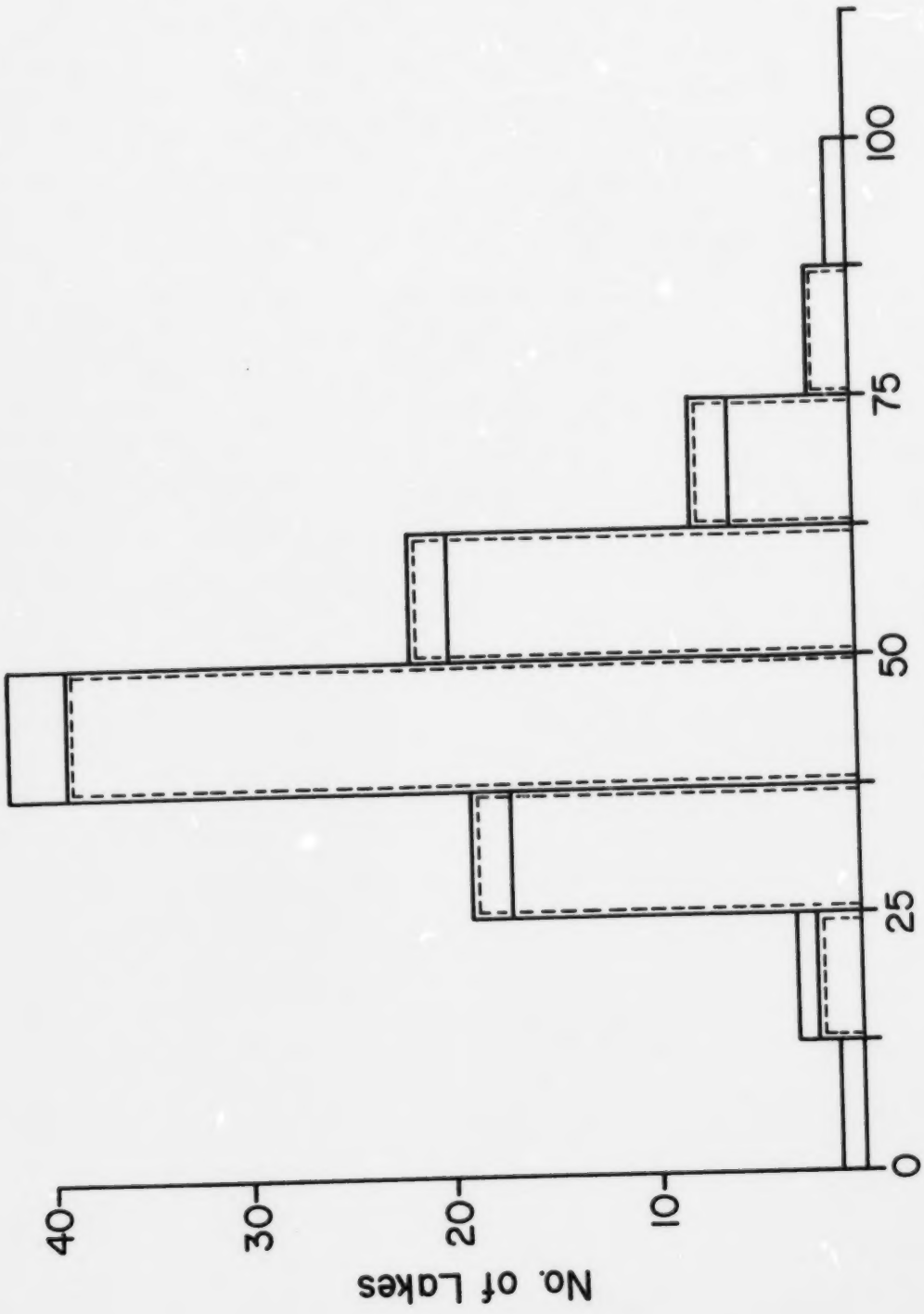

Fig. 2c. Frequency histogram of Cd. Legend as in Fig. 1.

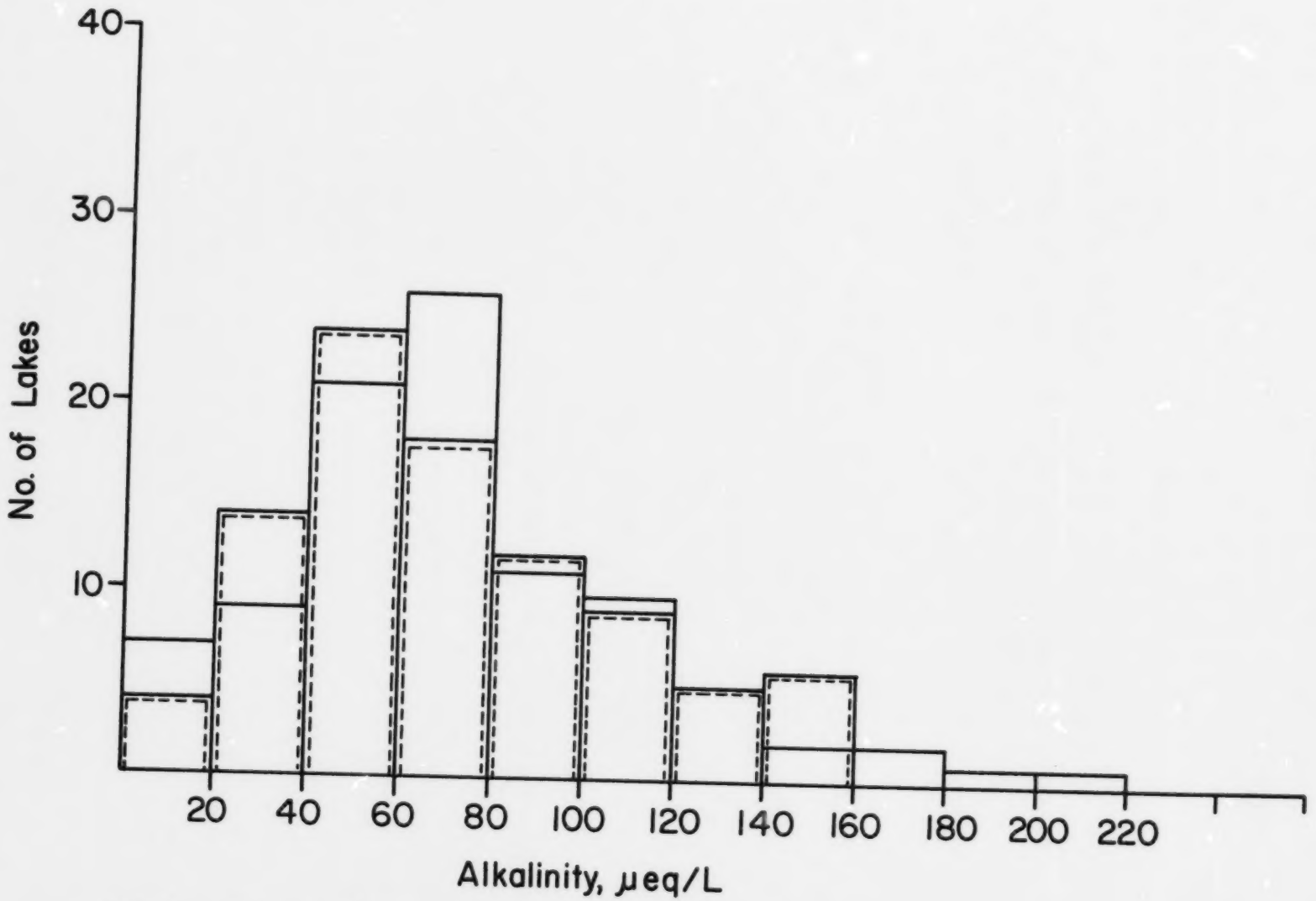

Fig. 2d. Frequency histogram of alkalinity. Legend as in Fig. 1.

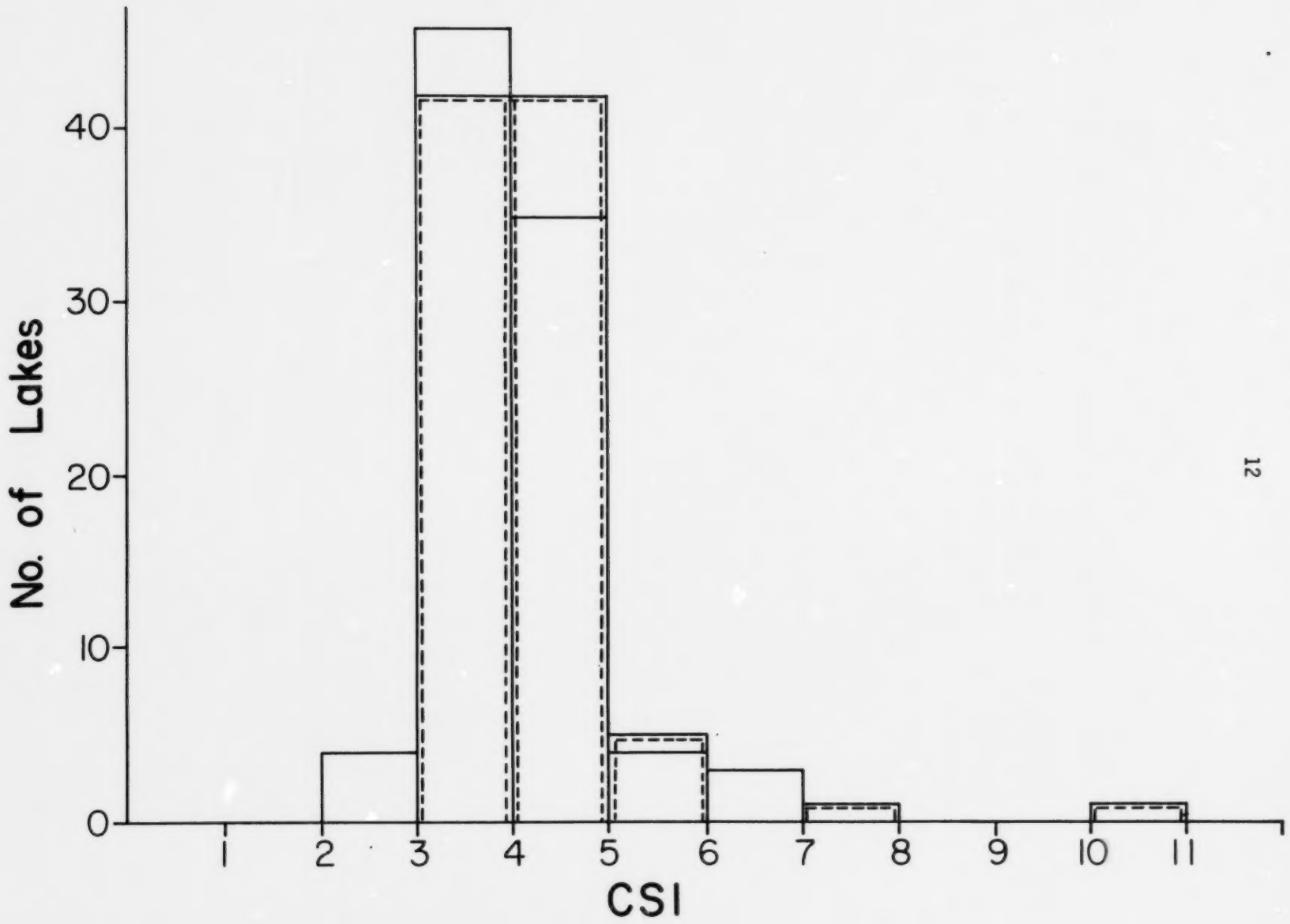
No. of Lakes
0
10
20
30
40
1
2
3
4
5
6
7
8
9
10
11
CSI

Fig. 2e. Frequency histogram of Δ51. Legend as in Fig. 2a.

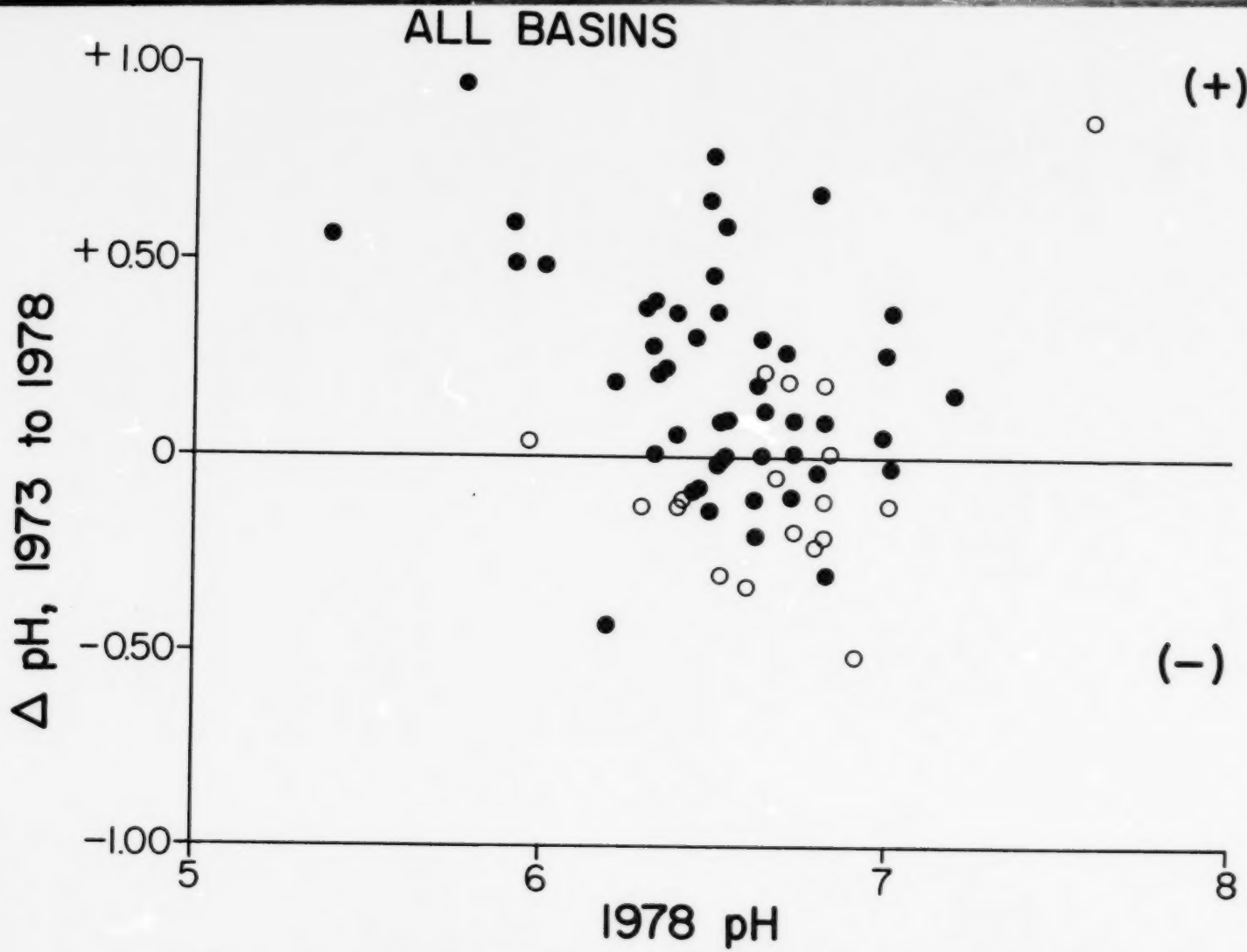

Fig. 3. Changes in pH from 1973 to 1978 plotted against the 1978 pH. Points above the zero line represent lakes which had higher readings in 1978 than in 1973. Points below the zero line represent lakes which had lower readings in 1978 than in 1973. o unmodified basins; • modified basins, as explained in the text.

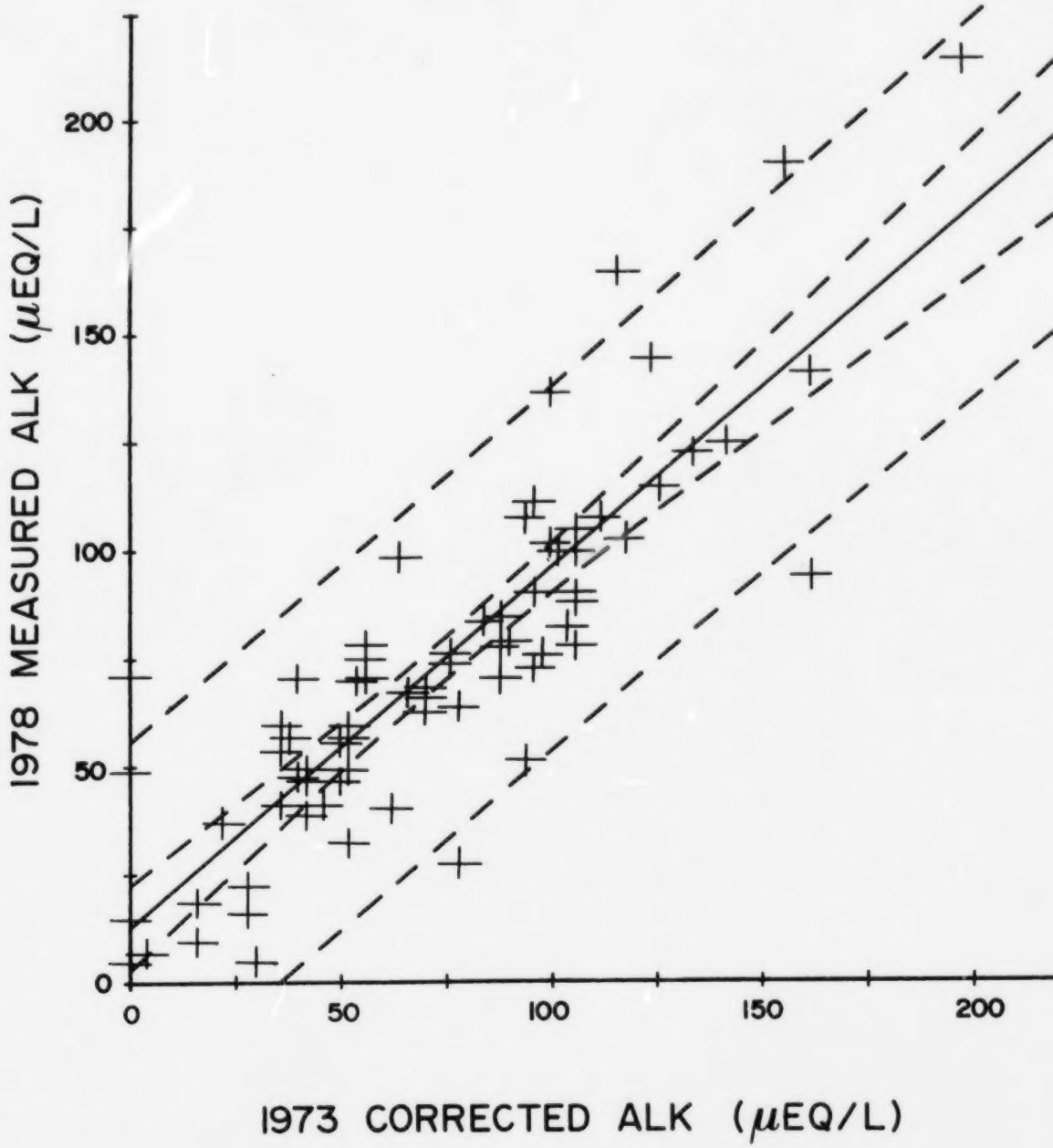

Fig. 4. A plot of measured 1978 alkalinities vs 1973 measured alkalinities as recalculated by G. A. McFarlane.

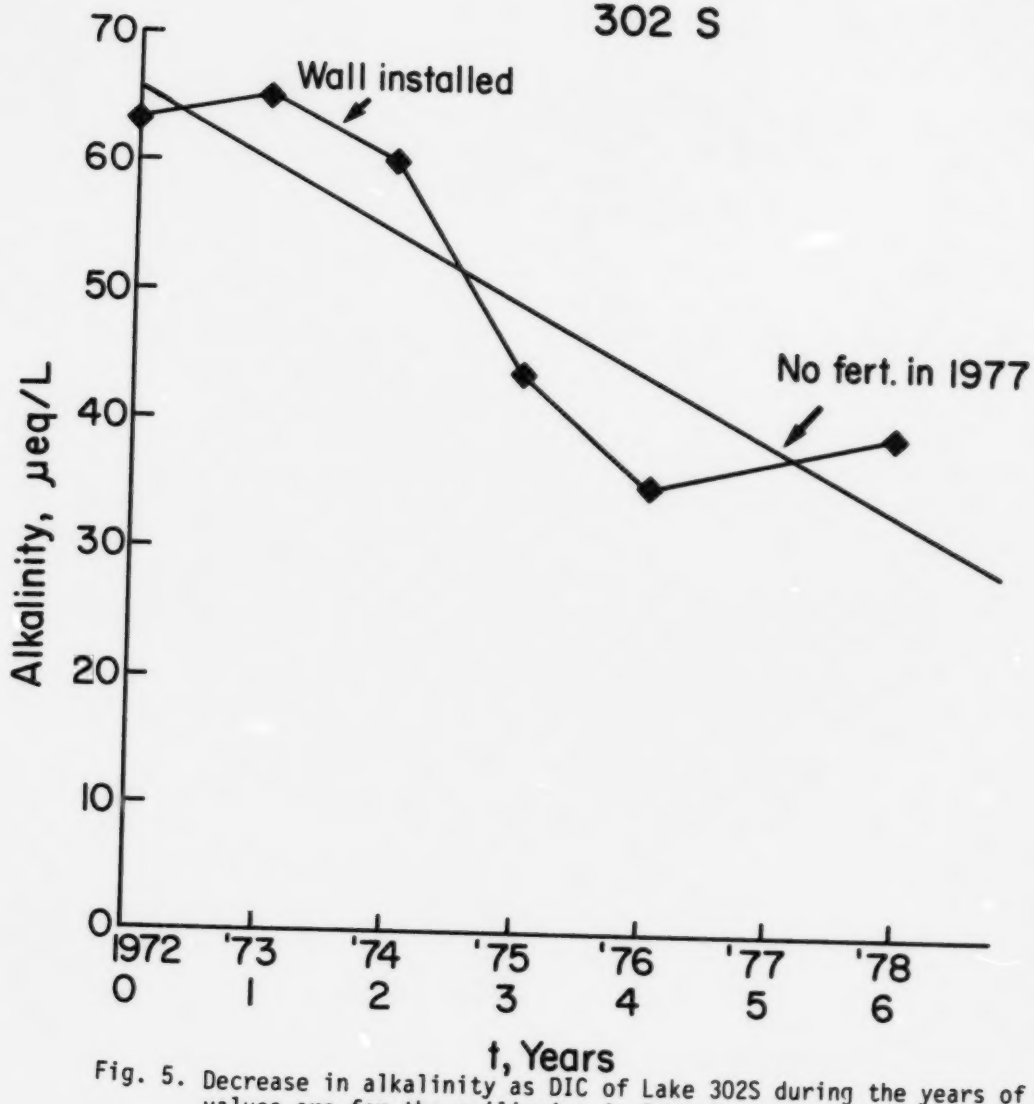

Fig. 5. Decrease in alkalinity as DIC of Lake 302S during the years of study. All values are for the epilimnion in late August or early September. The lake was fertilized in all years but 1977. The regression equation = -5.4t + 77 percent of the variance in observed data.

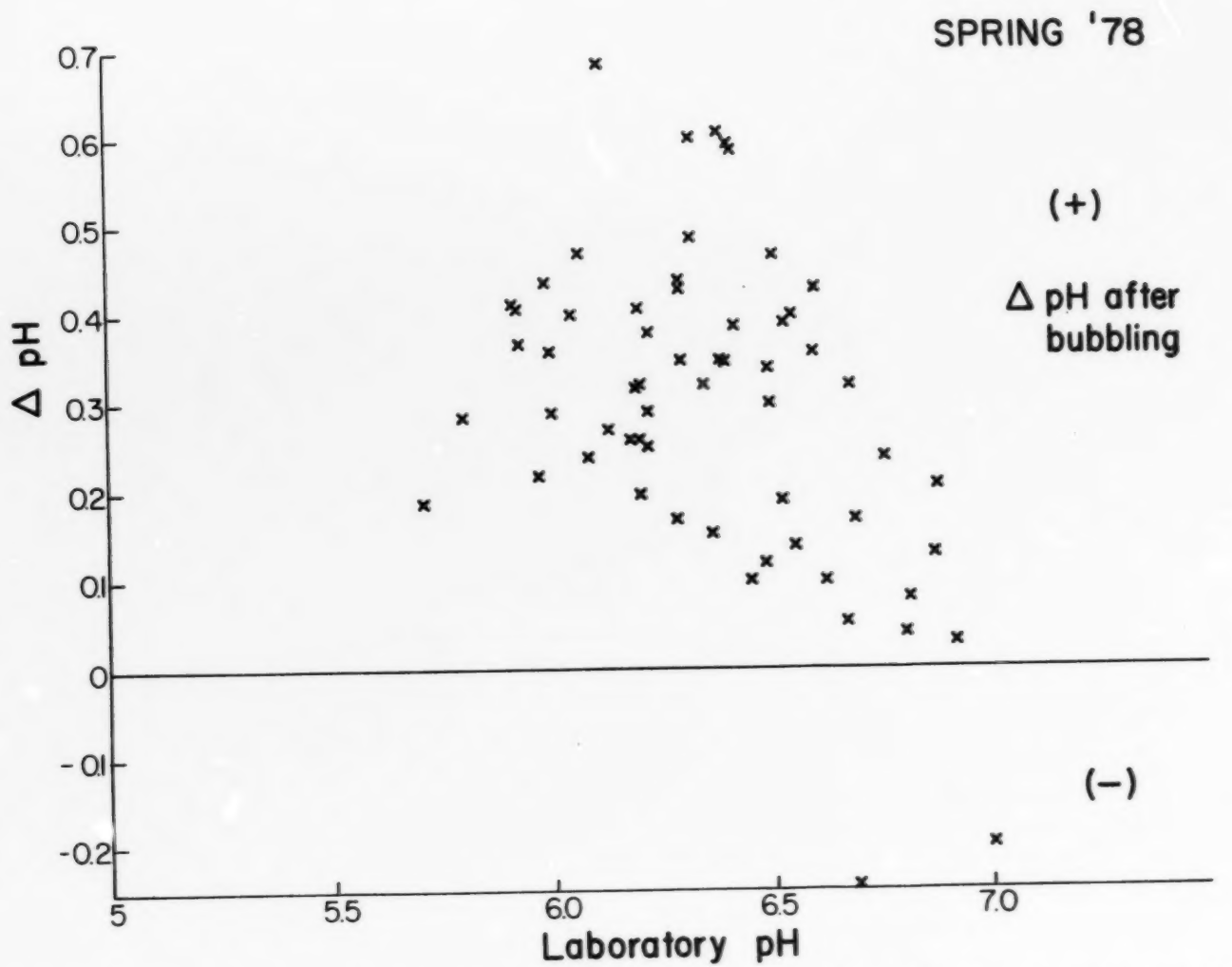

Fig. 6a. Change in pH of surface waters of surveyed lakes on bubbling to equilibrium with outside air. Spring 1978, when P_{CO_2} is generally above saturation.

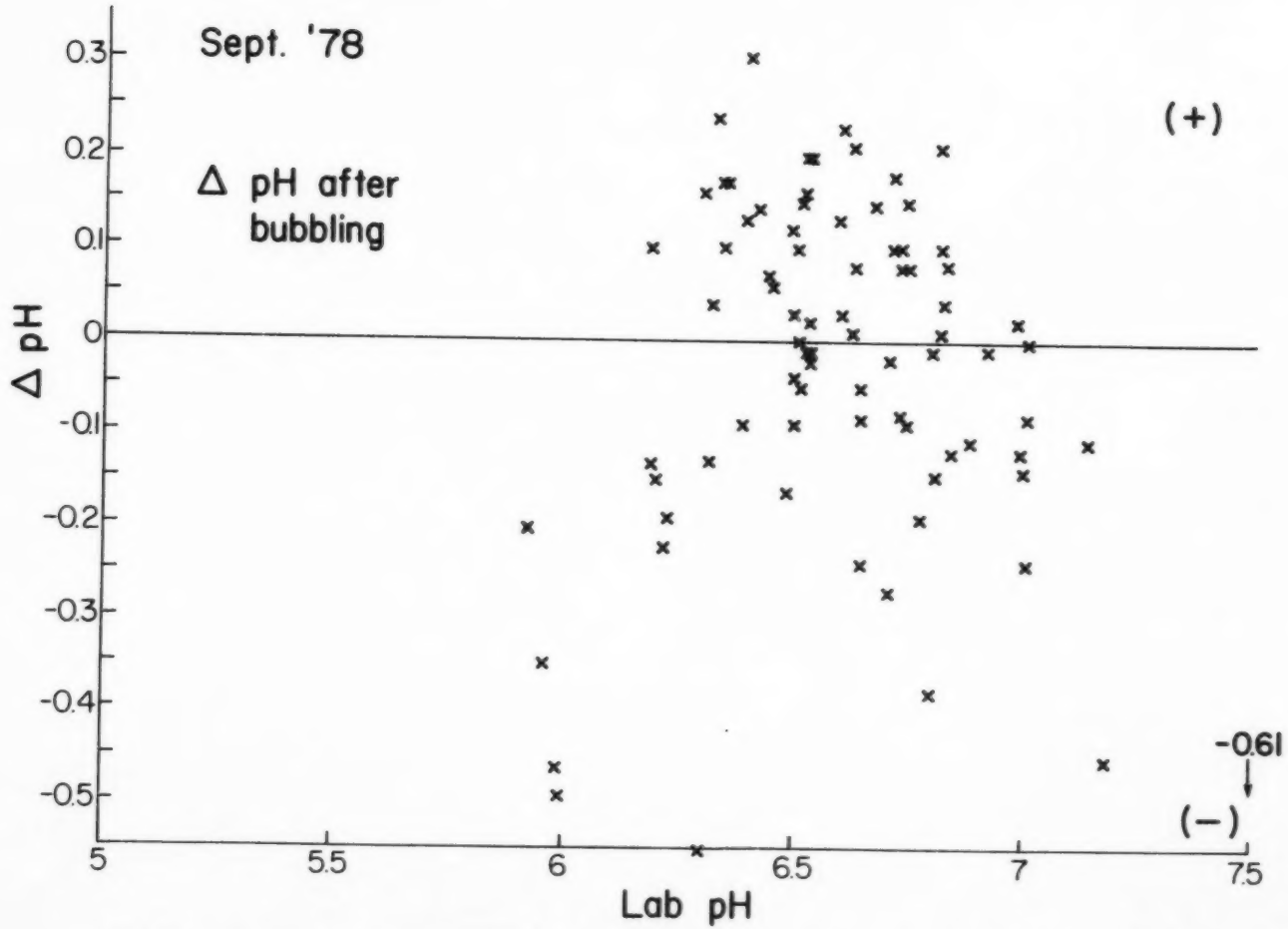

Fig. 6b. Change in pH of surface waters of surveyed lakes on bubbling to equilibrium with outside air. Late summer 1978, when P_{CO_2} may vary among lakes from undersaturation to supersaturation.

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